Long-range order and spin liquid states of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$

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Low-temperature states of polycrystalline samples of a frustrated pyrochlore oxide $Tb_{2+x}Ti_{2-x}O_{7+y}$ have been investigated by specific heat, magnetic susceptibility, and neutron scattering experiments. We have found that this system can be tuned from a long-range ordered state ($x > x_c$) to a spin-liquid state by a minute change of x. Specific heat shows a sharp peak at a phase transition at $T_c = 0.5$ K for $x = 0.005$. Inelastic neutron scattering shows that the crystal field ground state doublet of Tb^{3+} splits into two singlets below T_c, suggesting a cooperative Jahn-Teller transition due to a magneto-elastic coupling, accompanied by a small antiferromagnetic ordering.

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Magnetic systems with geometric frustration, a prototype of which is antiferromagnetically coupled Ising spins on a triangle, have been intensively studied experimentally and theoretically for decades[1]. Spin systems on networks of triangles or tetrahedra, such as triangular[2], kagomé[3], and pyrochlore[4] lattices, play major roles in these studies. Subjects that have fascinated many investigators in recent years are classical and quantum spin-liquid states[5–8], where conventional long-range order (LRO) is suppressed to very low temperatures. Quantum spin-liquids[6,7] in particular have been challenging both theoretically and experimentally since the proposal of the resonating valence-bond state[9]. The spin ice materials $R_2Ti_2O_7$ (R = Dy, Ho) are the well-known classical examples[5], while other experimental candidates found recently have been studied[10–12].

Among frustrated pyrochlore oxides[4], $Tb_2Ti_2O_7$ has attracted much attention because it does not show any conventional LRO down to 50 mK and remains in a dynamic spin-liquid state[13,14]. Theoretical considerations of the crystal-field (CF) states of Tb^{3+} and exchange and dipolar interactions of the system[15–17] showed that it should undergo a transition into a magnetic LRO state at about 1.8 K within a random phase approximation[17]. The puzzling origin of the spin-liquid state of $Tb_2Ti_2O_7$ is in hot debate[4,18–25]. An interesting scenario to explain the spin-liquid state is the theoretical proposal of a quantum spin-ice state[19]. More recently, another scenario of a two-singlet spin-liquid state was proposed to explain why inelastic neutron spectra in a low energy range are observed despite the fact Tb^{3+} is a non-Kramers ion[20,21].

Several experimental puzzles of $Tb_2Ti_2O_7$ originate from the difficulty of controlling the quality of single crystalline samples, resulting in strongly sample-dependent specific-heat anomalies at temperatures below 2 K[15,23,26–29]. In contrast, experimental results on polycrystalline samples are more consistent[13,14,23]. Among experimental results reported to date, an important clue to solve the puzzles seems to be a change of state at about 0.4 K suggested by specific heat[23], inelastic neutron scattering[23], and neutron spin echo[14] on polycrystalline samples. At this temperature, a few single-crystalline samples show a peak in the specific heat suggesting a phase transition[26,27], an issue that has not been pursued seriously. A possibility of a cooperative Jahn-Teller phase-transition well below 1 K was inferred many years ago from the observation of an anomalous temperature dependence of the elastic constants above 1 K[30]. The two-singlet spin-liquid scenario of Refs. 20, 21, and 31 is based on the assumption of a tetragonal lattice distortion in $Tb_2Ti_2O_7$ and the closely related ordered spin-ice compound $Tb_2Sn_2O_7$[32], but the accompanying lattice distortion might be too difficult to observe directly[22,33–36].

In the present work, we investigate the hypothesis that the non-stoichiometry x of $Tb_{2+x}Ti_{2-x}O_{7+y}$ is a tuning parameter for a quantum critical point separating a LRO state from a spin liquid state. We have therefore performed specific heat, magnetization, and neutron scattering experiments on polycrystalline samples of $Tb_{2+x}Ti_{2-x}O_{7+y}$ with different values of x. We find that a minute change of x brings about a systematic change of the specific heat. The ground state goes from LRO for $x > x_c$ to a spin liquid for $x < x_c$. Inelastic neutron scattering strongly suggests that this LRO is a cooperative Jahn-Teller lattice distortion accompanied by a small antiferromagnetic ordering. If this interpretation is correct, we may make a conjecture that the ground state for $x < x_c$ is a spin liquid state in which spin and lattice degrees of freedom are governed by quantum fluctuations.

Polycrystalline samples of $Tb_{2+x}Ti_{2-x}O_{7+y}$ with

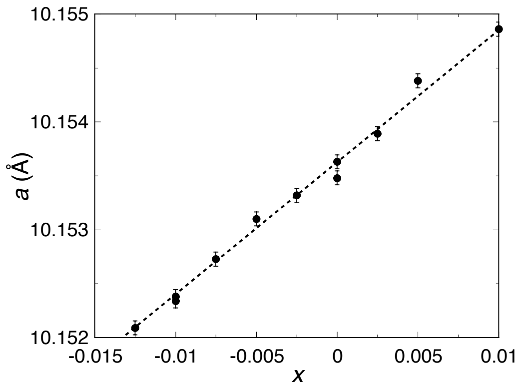

FIG. 1. Lattice constants of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ at 25 °C. The dashed line is a guide to the eye.

$-0.015 < x < 0.01$ were prepared by standard solid-state reaction[13]. The value of x was adjusted by changing the mass ratio of the two starting materials, Tb_4O_7 and TiO_2, which were heated in air at 1350 °C for several days with periodic grindings to ensure a complete reaction. It was ground into powder and annealed in air at 800°C for one day. The values of x used in this report are nominal, and have an offset about ±0.002. The value of y is determined by the oxidizing conditions. X-ray powder-diffraction experiments were carried out using a RIGAKU-SmartLab powder diffractometer equipped with a Cu $K_{\alpha 1}$ monochromator. The absence of impurity peaks in the powder diffraction patterns shows that the samples are single phase with pyrochlore structure[37]. To measure the x dependence of the lattice constant a at 25 °C, we performed θ-2θ scans on powder mixtures of $Tb_{2+x}Ti_{2-x}O_{7+y}$ and Si. Figure 1 shows that the lattice constant a has as a smooth variation with x, which ensures a continuous change of the stoichiometry of $Tb_{2+x}Ti_{2-x}O_{7+y}$ for small x.

Specific heat above 0.4 K was measured on a physical-property measurement-system. Measurements below 0.4 K were carried out using the quasi-adiabatic relaxation method on a dilution refrigerator[38]. DC magnetization measurements were carried out by a capacitive Faraday magnetometer in a ^{3}He refrigerator. Neutron powder diffraction measurements were performed on the triple-axis spectrometer CTAX at ORNL. Inelastic neutron scattering measurements were carried out on the time-of-flight spectrometer IN5 operated with $\lambda = 5$ and 10 Å at ILL. For these neutron scattering experiments, samples of $x = 0.005$ and -0.005 with weights of 5 and 9 g were mounted in a ^{3}He (CTAX) and a dilution refrigerator (IN5), respectively.

In Fig. 2 we show the specific heat C_P of the polycrystalline samples as a function of temperature together with a few previous measurements[23,26,39]. Earlier work have shown qualitatively similar results[40,41]. The $C_P(T)$ data show a systematic change by varying x. A sample with $x = 0.005$ shows a clear peak indicating a second-order phase transition at $T_c = 0.5$ K. Samples with $x = 0.0025$ and 0.000 show smaller peaks at 0.43 and 0.4 K, respectively. We note that C_P of the present sample with $x = 0.000$ agrees approximately with our previous measurements[23], the temperature range of which was extended down to 0.2 K in the present work on a sample (nominal $x' = 0$) prepared from a different commercial source of Tb_4O_7. Our previous interpretation[23] of the upturn below 0.5 K as a crossover behavior is incorrect owing to the insufficient temperature range. The previous C_P data[39] (Fig. 2) on a polycrystalline sample with their nominal $x'' = 0$ corresponds to our $x = -0.0125$, implying that fine tuning of x requires careful sample preparation. In the inset of Fig. 2, we show a cumulative phase diagram constructed from $C_P(T, x)$ in conjunction with the susceptibility and neutron scattering experiments discussed below.

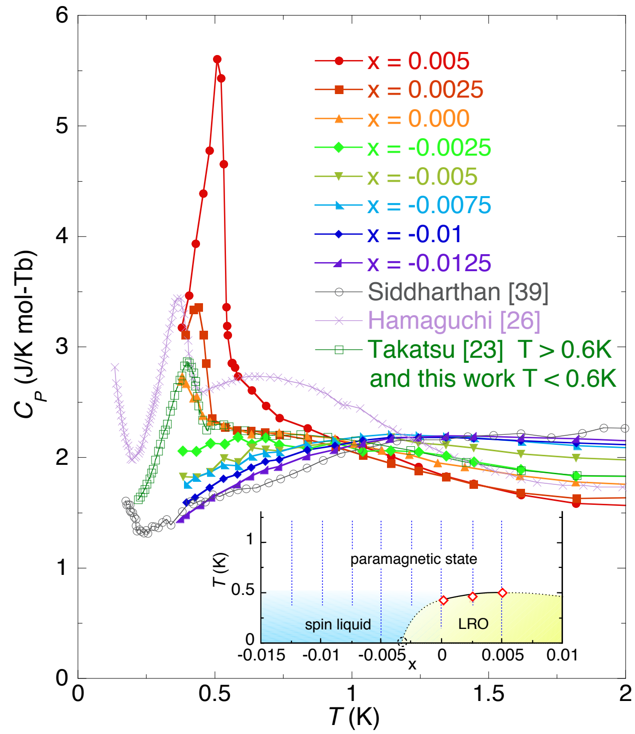

FIG. 2. (Color online) Temperature dependence of the specific heat of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$. Previous measurements of poly- and single-crystalline samples[23,26,39], as well as the present measurements below 0.6 K of a sample prepared in the same manner as in Ref. 23, are plotted for comparison. The inset shows a phase diagram expected from the specific heat, susceptibility, and neutron scattering.

A peak of $C_P(T)$ in $Tb_2Ti_2O_7$ was first reported for a single-crystalline sample at 0.37 K[26]. These $C_P(T)$ data[26], reproduced in Fig. 2, show significantly different T dependence from any of the polycrystalline samples. The sharp peak at 0.37 K may result from a portion of

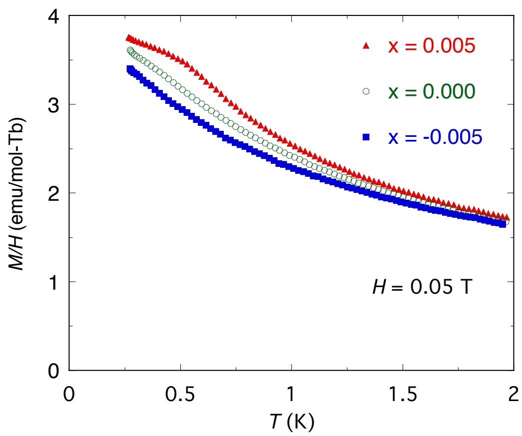

FIG. 3. (Color online) Temperature dependence of the magnetic susceptibility of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ with $x = -0.005$, 0.000, and 0.005.

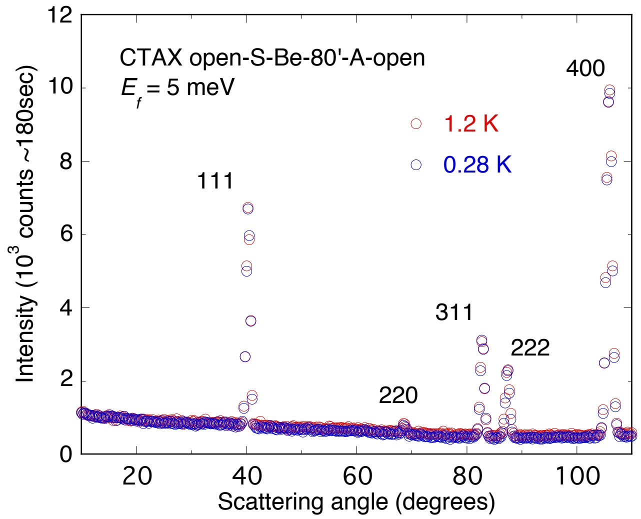

FIG. 4. (Color online) Neutron powder diffraction pattern of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ with $x = 0.005$ taken above and below $T_c = 0.5$ K.

the sample having a non-stoichiometry parameter around $x = -0.001$, corresponding to a peak slightly lower in temperature than our $x = 0.000$. However, a hump in $C_P(T)$ around 0.75 K for the single crystal does not appear for the polycrystalline samples. We believe that these single- and poly-crystalline samples have significant, but presently not well understood, differences in quality.

In order to check whether T_c is an antiferromagnetic transition, as suggested in Ref. 26, we performed magnetization and neutron powder-diffraction experiments. In Fig. 3 we show the magnetic susceptibility as a function of temperature for three polycrystalline samples with $x = \pm 0.005$ and 0.000. The susceptibilities for $x = 0.005$ and 0.000 show only slight anomalies around the clear peaks of $C_P(T)$ at $T_c = 0.5$ and 0.4 K, respectively. These results are very different from typical behavior expected of antiferromagnetic phase transitions.

In Fig. 4 we show neutron powder-diffraction patterns for the $x = 0.005$ sample below and above T_c. The pattern below T_c shows neither any clear antiferromagnetic reflections nor any clear changes due to a structural transition. A rough estimate of the upper limit of the antiferromagnetic ordered moment is about 0.1 μ_B. The intensity of the sloping paramagnetic scattering, a background for Bragg peaks, decreases slightly as temperature is lowered from 1.2 to 0.28 K. This is brought about by a change in the magnetic excitations. The lack of obvious antiferromagnetism distinctly separates $Tb_2Ti_2O_7$ from the ordered spin-ice compound $Tb_2Sn_2O_7$[32,42], in which antiferromagnetic ordering with a moment of 5.9 μ_B was observed well below $T_c = 0.87$ K.

To study the spectral change of the magnetic excitations through T_c, we performed inelastic neutron scattering measurements using the spectrometer IN5[43] with an energy resolution of $\Delta E = 0.01$ meV (FWHM), which is 6 times better than in a previous study[23]. Figure 5 shows the temperature dependence of an energy spectrum for the $x = 0.005$ sample at $Q = 0.6$ Å^{-1}. It is evident that the spectrum changes from a continuum ($T > T_c$) to a peaked structure at 0.1 meV ($T < T_c$). Since the peak at 0.1 meV is essentially dispersionless and Q independent, the excitation is probably due to a CF splitting of the ground state doublet by a lowering of the local trigonal symmetry. As pointed out in Refs. 20, 21, and 31, a splitting of the CF ground-state doublet into two singlets is the simplest evidence of a Jahn-Teller distortion due to a magneto-elastic coupling. Therefore, the evolution of the 0.1 meV excitation strongly suggests that T_c is a Jahn-Teller structural phase transition inferred in Ref. 30. An energy spectrum of the $x = -0.005$ sample is also shown in Fig. 5 for comparison, revealing quantum fluctuations with an energy scale of 0.1 meV.

The high sensitivity of IN5 enabled us to observe a small Bragg peak, being undetectable in the CTAX data (Fig. 4). In the inset of Fig. 5, the intensity of the elastic scattering for $|E| < 0.005$ meV is plotted as a function of Q. Below T_c, a clear Bragg peak at $Q = 0.54$ Å^{-1} is observed, which can be indexed as $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. Although this peak could be of a nuclear (structural) origin, it is more likely an antiferromagnetic reflection. In fact, two recent neutron scattering experiments carried out on single-crystalline samples of $Tb_2Ti_2O_7$ show magnetic short-range-order around the same $\boldsymbol{Q} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$[21,25]. A rough estimate of the antiferromagnetic ordered moment is 0.08 μ_B. We note that the Q-width of the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peak is somewhat larger than the coarse Q resolution on IN5. Whether this peak is truly long-range order would have to await high-resolution neutron diffraction measurements, which are difficult in view of the small moment.

The previously reported transition or crossover at about 0.4 K for the poly- and single-crystalline

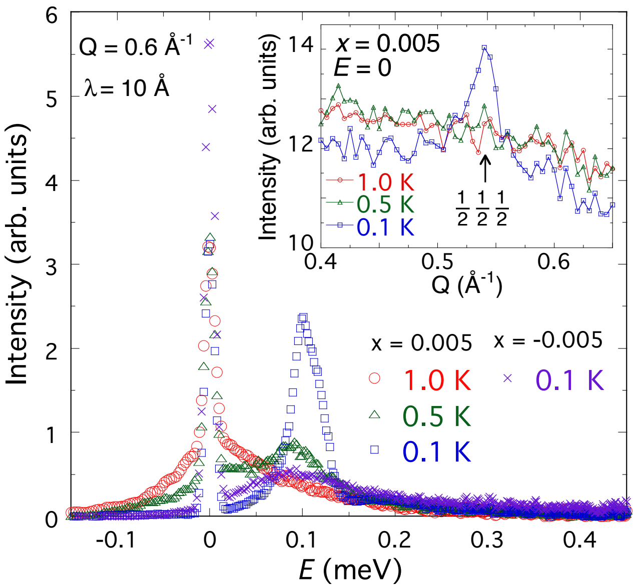

FIG. 5. (Color online) Energy spectra of inelastic neutron scattering for polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ with $x = 0.005$ and -0.005. The inset shows the Q dependence of the elastic scattering for the $x = 0.005$ sample around $Q = |(\frac{1}{2}\frac{1}{2}\frac{1}{2})|$ above and below T_c.

$Tb_2Ti_2O_7$[14,23,26] is presumably attributable to the same origin as that of the present $x = 0.005$ sample. The clear 0.1 meV excitation peak for this sample is most simply accounted for by a Jahn-Teller distortion and resultant CF splitting. Since this is an indirect evidence for the structural transition, more direct observation, by X-ray diffraction e.g., remains to be performed, but such measurements at low temperatures are exceedingly difficult. By assuming a Jahn-Teller distortion ($T \ll T_c$), an expansion of the theoretical framework of Refs. 20, 21, and 31 may be a promising direction to explain the ground state of the polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ with $x > x_c$, especially for the analysis of inelastic neutron scattering data. In order to reproduce the phase transition at $T_c > 0$, the theory[20,21,31] will have to be modified to include a soft phonon mode and a spin-lattice coupling. Along this line, the long-standing puzzle of the spin liquid state of $Tb_2Ti_2O_7$ may be reformulated to a novel problem of frustration having both spin and lattice degrees of freedom; Why and how do the spins and the soft phonon modes fluctuate quantum mechanically down to $T = 0$ for $x < x_c$?

In summary, we have investigated the low-temperature states of polycrystalline $Tb_{2+x}Ti_{2-x}O_{7+y}$ samples by specific heat, magnetic susceptibility, and neutron scattering experiments. We have found that this system can be tuned by a minute change of the parameter x from a LRO ground state for $x > x_c$ to a liquid-type ground state with spin- and possibly lattice-fluctuations for $x < x_c$. Specific heat shows a sharp peak at a second-order phase-transition T_c for $x > x_c$. Inelastic neutron scattering shows that the CF ground doublet splits into two singlets below T_c, suggesting strongly that T_c is a cooperative Jahn-Teller structural transition accompanied by a small antiferromagnetic ordering with a wave-vector $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$.

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